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Nickel-Catalyzed Allylic Substitution of Simple Alkenes

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On the occasion of the 150th anniversary of Department of Chemistry, The University of Tokyo

Abstract: This report describes a nickel-catalyzed allylic substitution process of simple alkenes whereby an important structural motif, a 1,4-diene, was prepared. The key to success is the use of an appropriate nickel–phosphine complex and a stoichiometric amount of silyl triflate. Reactions of 1-alkyl-substituted alkenes consistently provided 1,1-disubstituted alkenes with high selectivity. Insight into the reaction mechanism as well as miscellaneous application of the developed catalytic process is also documented.

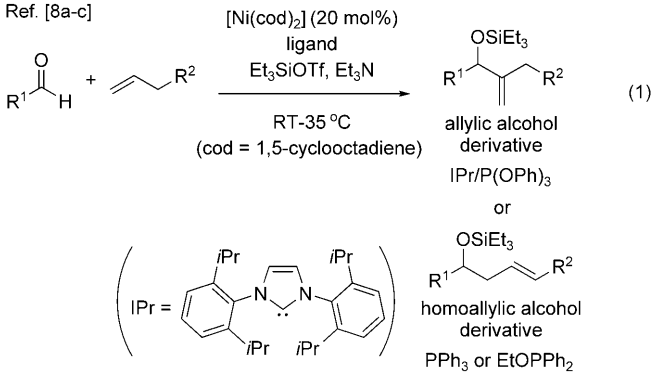
Keywords: alkenes · allylic substitution · homogeneous catalysis · nickel · reaction mechanisms

Introduction

Simple terminal alkenes are produced in metric megaton amounts each year, and they are inexpensive feedstock chemicals that serve as starting materials for the preparation of many classes of organic compounds.[1] Therefore, catalytic processes that convert simple terminal alkenes into more valuable compounds with concomitant C–C bond formation are highly desirable, such as the polymerization of alkenes[2] and hydroformylation.[3] In these transformations, the alkene double bonds in the starting materials are converted into C–C single bonds. In contrast, olefin cross metathesis,[4] the Heck reaction[5] and the carbonyl-ene reaction[6] are widely used catalytic reactions of terminal alkenes that lead to compounds bearing C=C double bonds. The Heck reaction and carbonyl-ene reaction, however, commonly employ conjugated terminal alkenes and electron-rich alkenes, respectively, especially in intermolecular variants; simple alkenes, such as alpha-olefins, are rarely used in these reactions.

In a pioneering paper in 2004, Ogoshi and co-workers reported intramolecular, nickel-mediated cyclization of alkenals in the presence of organophosphine and trimethylsilyl triflates (Me_3SiOTf),[7a] and shortly thereafter we reported nickel-catalyzed intermolecular three-component couplings of alkenes, aldehydes, and silyl triflates.[8a] Over the past several years, both of our groups have actively investigated other related transformations.[7–9] In our ongoing efforts in this area, we have developed highly regioselective nickel-catalyzed three-component couplings of alkenes, aldehydes, and silyl triflates, thus enabling the access to both homoallylic alcohols[8b] and allylic alcohols[8c] by judicious choice of reaction conditions [Eq. (1)]. Nickel-catalyzed intermolecular coupling reactions of simple terminal alkenes with α,β-unsaturated carbonyl compounds have also been reported [Eq. (2)].[8d] In these reactions, simple terminal alkenes serve as carbon nucleophiles under mild reaction conditions. The resulting functionalized alkenes can be employed as versatile building blocks for subsequent manipulations.

The transition-metal-catalyzed allylic substitution reactions (ASRs) provide a highly valuable tool in organic synthesis.[10] This methodology accommodates a wide range of



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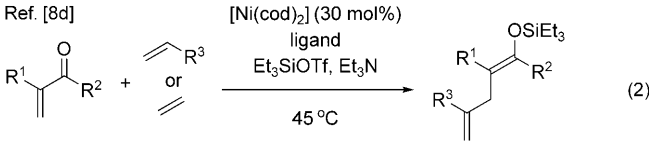

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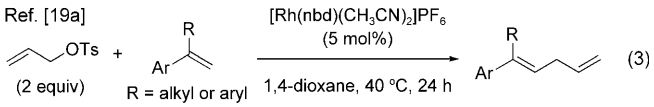
carbon nucleophiles, such as activated methylene compounds,[11] enolates,[12] enamines,[13] Grignard reagents,[14] organozinc reagents,[15] and alkenyl[16] or aryl[17] boron reagents. ASR of terminal alkenes, in principle, would enable the construction of 1,4-dienes ("skipped" dienes), a key structural motif prevalent in natural products.[18] Intermolecular allylic substitution reactions with non-metalated terminal alkenes, were reported by Tsukada et al.,[19] in which only conjugated alkenes, styrene derivatives, and butylacrylate were employed [Eqs. (3) and (4)]. Catalytic intramolecular ASRs of simple terminal alkenes were studied extensively by Oppolzer et al. with various transition-metal catalysts [Eq. (5)].[20] However, catalytic intermolecular ASR of simple terminal alkenes had not been reported before we started our investigation.[21]



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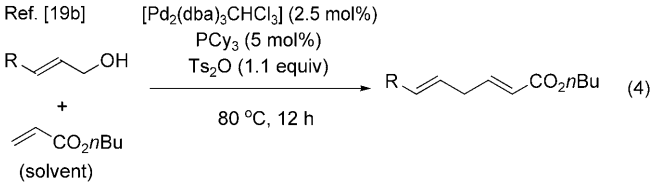

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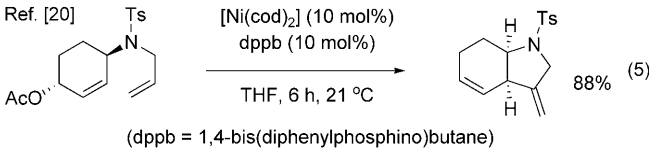

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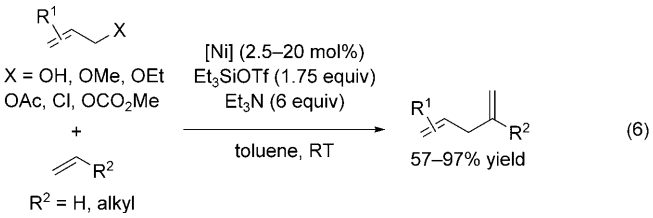
In 2010, we described the first catalytic intermolecular ASR of simple alkenes.[22] In this process, several allylic alcohol derivatives were shown to react with terminal alkenes, including ethylene and propylene, in the presence of a catalytic amount of a nickel complex and a stoichiometric amount of an activator, triethylsilyl triflate, to give a variety of 1,4-dienes in high yield [Eq. (6)]. These reactions proceeded to completion at room temperature in less than 18 hours. An attractive feature of this process is the high branched-to-linear ratios in favor of 1,1-disubstituted alkenes when 1-alkyl-substituted alkenes are used. In this article, we describe the details of the developed nickel-catalyzed allylic substitution reactions including experiments that provide insight into the mechanism of this transformation, as well as a variety of its applications.



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Results and Discussion

Nickel-Catalyzed Allylic Substitution of Ethylene

We initiated our research utilizing ethylene and a nickel catalyst, and found that the use of a stoichiometric amount of Lewis acid, Et_3SiOTf, is indispensable for the ASR of ethylene to proceed. As is often the case with transition-metal-catalyzed processes, the choice of phosphine ligand was found to have a profound impact. The effect of the phosphine ligand in the nickel-catalyzed ASR (10 mol%) of ethylene (1 atm) with cinnamyl methyl carbonate (**1a**) is summarized in Table 1, in which the results are arranged according to the cone angle of the ligand.[23]

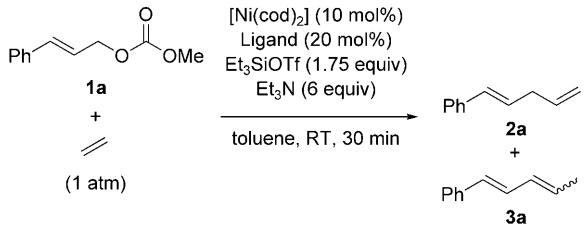
While a significant gap between conversion and yield of **2a** was observed in most cases, probably due to decomposition of **1a** in the presence of Et_3SiOTf, high yields were obtained when $PCyPh_2$ and $P(o\text{-anisyl})_3$ (anisyl = $MeOC_6H_4$) were used. In all cases, a small amount of conjugated diene **3a** was observed as an inseparable side product.[24] At this stage in our investigations, there was no clear correlation between steric or electronic factors of the phosphine ligand and the product yield.

With the optimal reaction conditions in hand, we then turned our attention to the scope of the leaving group of the allylic alcohol derivatives (Table 2). In contrast to typical palladium-catalyzed ASRs using allylic carbonates, allylic esters, and allylic chlorides as coupling partners for an alkene, ethylene undergoes substitution with a wide range of allylating reagents, including electrophiles bearing classically poor leaving groups such as alkyl ethers,[25] trimethylsilyl ethers, and even allylic alcohols[26] (entries 1–4). Et_3SiOTf is proposed to activate such allylic alcohol derivatives bearing classically poor leaving groups toward oxidative addition (see below). Cinnamyl derivatives bearing OAc and chloride as a leaving group also performed well in this transformation (entries 5, 6). It is noteworthy that in

Abstract in Japanese:

我々は、ニッケルを触媒として用いる単純アルケンのアリル位置換反応を新たに開発した。本手法を用いると重要な官能基として知られる1,4-ジエンを得ることができる。本反応では、適切なリン配位子を有するニッケル錯体を触媒とし、量論量のシリルトリフラートを用いることが重要である。末端アルケンを基質として用いると、高い選択性で1,1-二置換アルケンが生成物として得られた。反応機構に関する考察と本反応の応用についても述べる。

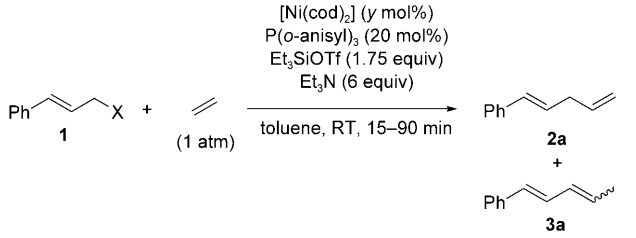
Table 1. Ligand screening for nickel-catalyzed allylic substitution of ethylene.



Ligand[a]	Cone angle [°][b]	ν_{CO} [cm^{-1}][c]	Conv. [%][d]	Yield of **2a** [%][e]	Yield of **3a** [%][e]
PMe_3	118	2064.1	42	3	4
PMe_2Ph	122	2065.3	37	5	trace
$P(OEt)Ph_2$	133	2071.6	93	30	2
PPh_3	145	2068.9	25	4	trace
P(*p*-anisyl)$_3$	145	2066.1	71	48	1
$PCyPh_2$	153	(2064.8)[g]	100	89	trace
PCy_2Ph	162	(2060.6)[g]	47	26	trace
PCy_3	170	2056.4	43	13	trace
P(*o*-tolyl)$_3$	194	2066.6	38	11	trace
P(*o*-anisyl)$_3$	(>194)[f]	2058.3	100	90	6

[a] Abbreviations: Cy = cyclohexyl; tolyl = MeC_6H_4; anisyl = $MeOC_6H_4$. [b] Ref. [23]. [c] The stretching frequencies (ν_{CO}) of the terminal CO of $[Ni(CO)_3\mathbf{L}]$ in CH_2Cl_2. Ref. [23]. [d] Determined by GC. [e] Yields were determined by ^{1}H NMR spectroscopic analysis using 1,4-dioxane as an internal standard. [f] Estimated values. [g] Calculated values using Tolman's equation. Ref. [23].

Table 2. Scope of leaving group and decrease of catalyst loading in nickel-catalyzed ASR.



Entry	X	*y*	Yield of **2a**[a]	Yield of **3a**[a,b]
1	OMe (**1b**)	10	91	5
2	OEt	10	85	4
3[c]	$OSiMe_3$	10	75	trace
4[d]	OH	20	56	<5
5	OAc	10	86	10
6	Cl	10	63	20
7	OCO_2Me	2.5	71	26
8[e]	OCO_2Me	2.5	91	7

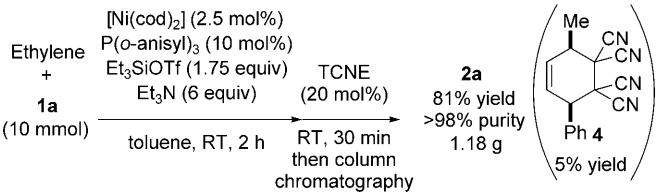
[a] Yields were determined by ^{1}H NMR spectroscopic analysis using acetonitrile as an internal standard. [b] For **3a**, *E*/*Z* = approx 3:1 in all cases. [c] Me_3SiOTf (1.75 equiv) used in place of Et_3SiOTf, 4 h. [d] Me_3SiOTf (3 equiv) used instead of Et_3SiOTf. [e] 10 mol% of P(*o*-anisyl)$_3$ used, 3 h.

any studied case no reaction occurred in the absence of silyl triflate.

Further decreases in the catalyst loading from 10 mol% resulted in low selectivity of **2a** over **3a**. When 2.5 mol% of $[Ni(cod)_2]$ and 5.0 mol% of P(*o*-anisyl)$_3$ were used (entry 7), the formation of desired product **2a** (71% yield) was accompanied by a significant amount of **3a** (26% yield). Extensive studies to overcome this issue revealed that the use of an excess amount of P(*o*-anisyl)$_3$ suppresses the formation of **3a**. When 2.5 mol% of $[Ni(cod)_2]$ and 10 mol% of P(*o*-anisyl)$_3$ (Ni/phosphine 1:4) were used (entry 8), **2a** was obtained in 91% yield accompanied by a small amount of **3a** (7% yield).[27] The reason for the increased selectivity when an excess amount of phosphine ligand is as yet unclear.

The scope of the nickel-catalyzed ASR of ethylene regarding allylic alcohol derivatives was next examined (Table 3). Both (*Z*)-cinnamyl methyl ether (**1c**) and the corresponding branched isomer **1d** provided linear product **2a** in good yield with complete *E* selectivity (entries 2, 3). A broad range of allylic alcohol derivatives functioned well (entries 4–8). When substrates bearing alkyl substituents were used, a small amount of branched products was observed (entries 5–8). To our delight, substituents at any position of the allyl carbonate were tolerated, as demonstrated in entries 9–11.

A drawback of the nickel-catalyzed ASR of ethylene was the formation of a small amount of conjugated 1,3-dienes, which as noted above were difficult to separate from the desired 1,4-diene products by standard chromatographic purification. On the expectation that 1,3-dienes would react with dienophiles in a [4+2] cycloaddition to give a separable cycloadduct, a variety of common dienophiles were examined by using a mixture of **2a** and **3a** obtained from nickel-catalyzed ASR of ethylene with **1a**. While acrylate, acrolein, acryloyl chloride, and maleic anhydride failed to react with **3a** at room temperature regardless of the presence of Et_3SiOTf, a commercially available dienophile, tetracyanoethylene (TCNE),[28] readily reacted with (*E*)-**3a** selectively and quantitatively at room temperature without Lewis acid, to afford the corresponding cycloadduct **4**. The desired product **2a** was not affected by TCNE and could be isolated with >98% purity (a tiny amount of (*Z*)-**3a** was included). With a convenient purification method of **2a** in hand, nickel-catalyzed ASR of ethylene with **1a** was conducted on a 10 mmol scale as a demonstration of the scalability of this



Scheme 1. Gram-scale allylic substitution reaction of ethylene.

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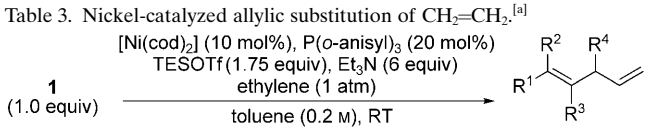
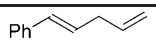
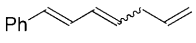
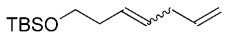
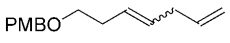
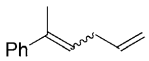
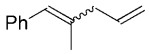
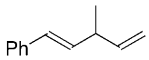
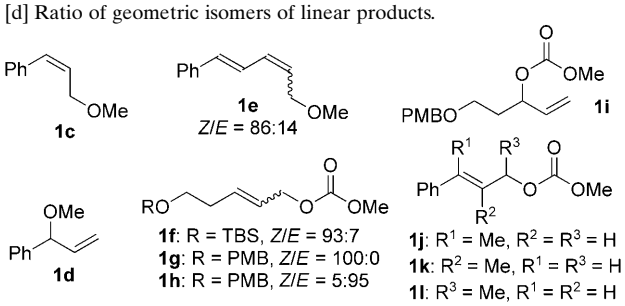
Table 3. Nickel-catalyzed allylic substitution of $CH_2{=}CH_2$.[a]



Entry	Substrate	Product	Yield[b] [%]	l/b[c]	E/Z[d]
1	**1b**	 **2a**	75	>99:1	>99:1
2	**1c**	**2a**	83	>99:1	>99:1
3	**1d**	**2a**	74	>99:1	>99:1
4	**1e**	 **2b**	84	>99:1	83:17
5	**1f**	 **2c**	97	95:5	94:6
6	**1g**	 **2d**	73	98:2	92:8
7	**1h**	**2d**	82	98:2	92:8
8	**1i**	**2d**	76	98:2	92:8
9	**1j**	 **2e**	57	>99:1	94:6
10	**1k**	 **2f**	81	>99:1	88:12
11	**1l**	 **2g**	71	>99:1	>99:1

[a] A solution of $[Ni(cod)_2]$ (10 mol%) and P(*o*-anisyl)$_3$ (20 mol%) in toluene (0.2 M) was purged with ethylene, and the ethylene atmosphere was maintained with an ethylene balloon. Et_3N (6 equiv), allylic alcohol derivative (1 equiv), and Et_3SiOTf (1.75 equiv) were then added, and the reaction was stirred at RT. Abbreviations: TBS = *tert*-butyldimethylsilyl; PMB = *p*-$MeOC_6H_4CH_2$. [b] Isolated yield. [c] Linear/branched product. [d] Ratio of geometric isomers of linear products.



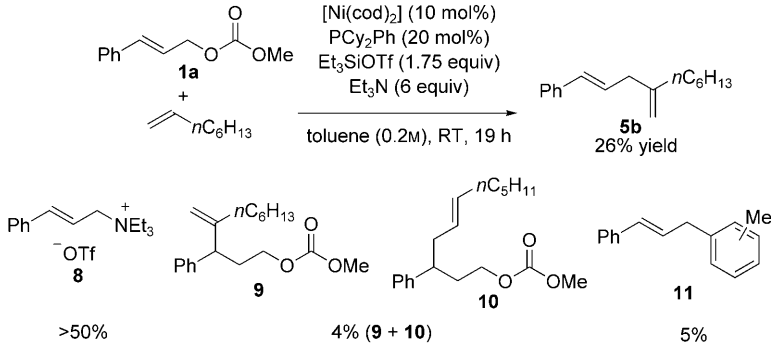
transformation (Scheme 1). The reaction was conducted under the same conditions as optimized on the small scale reaction. Filtration of the reaction mixture through a pad of silica gel and treatment with TCNE followed by chromatographic purification provided the desired coupling product **2a** in 81% yield (1.18 g) with >98% purity.

Nickel-Catalyzed Allylic Substitution of 1-Substituted Simple Alkenes

We next examined the nickel-catalyzed ASR of 1-substituted alkenes, commencing with the gaseous alpha-olefin propylene. It was clear from initial studies that regioselectivity may be a concern when using 1-substituted olefins. Nickel-catalyzed ASR of propylene (1 atm) with cinnamyl methyl carbonate (**1a**) afforded a mixture of **5a**, **6**, and **7** in favor of 1,1-disubstituted olefin **5a** (Table 4). Yield and selectivity of ASR were found to be strongly dependent on the phosphine ligand employed. The effect of the phosphine ligand on yield and selectivity is summarized in Table 4, in which the results are arranged in order of steric bulkiness of phosphine ligand.

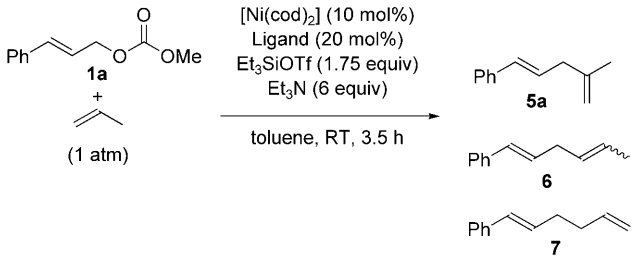
Product yield is influenced strongly by the steric demand of the phosphine ligand. While relatively large (θ (cone angle) > 170°) and small (θ < 145°) phosphine ligands provided no product, the reactions proceeded well using medium-sized phosphine ligands (145° < θ < 170°). An exception to this trend was P(*o*-anisyl)$_3$, which afforded the ASR products in high yield despite its large cone angle (estimated to be θ > 194°).[29] In addition to product yield, regioselectivity for the 1,1-disubstituted olefin **5a** also appears to be positively correlated with the steric bulkiness of the phosphine ligand, that is, the bulkier the phosphine ligand, the higher the selectivity. P(*o*-anisyl)$_3$ is again an exception to this rule. These observations and trends are discussed in further detail below. Taking into consideration a balance of yield and selectivity, commercially available PCy_2Ph was determined to be the optimal ligand (77% yield, **5a**/**6**/**7** = 98:1:1).

Encouraged by the results of propylene, a higher boiling alpha-olefin (i.e., not a gas at standard temperature and pressure (STP)), 1-octene, was used as a substrate in the nickel-catalyzed ASR. The desired product **5b**, however, was obtained in low yield under the conditions optimal for a reaction of propylene (Scheme 2). In addition to **5b**, several byproducts **8**–**11** were obtained, among which triethylamine adduct **8** was the major byproduct (>50% yield). It was found that the formation of major byproduct **8** is mediated by Et_3SiOTf and that nickel catalyst is not necessary for the formation of **8**.



Scheme 2. Initial trial of ASR of 1-octene.

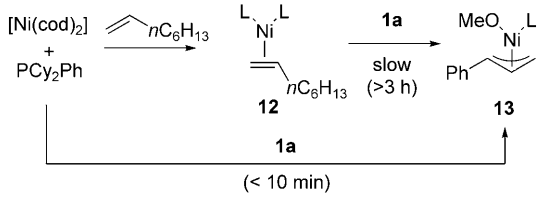
Table 4. Ligand screening for ASR of propylene.



Ligand	Cone angle [°][a]	ν_{CO} [cm^{-1}][b]	Yield [%][c]	Selectivity (**5a**/**6**/**7**)[d]
PMe_3	118	2064.1	0	–
PMe_2Ph	122	2065.3	0	–
$P(OEt)Ph_2$	133	2071.6	trace	–
PPh_3	145	2068.9	0	–
$P(p\text{-anisyl})_3$	145	2066.1	37	77:7:16
$PCy(p\text{-F-}C_6H_4)_2$	(153)[e]	(2066.2)[f]	64	91:1:8
$PCyPh_2$	153	(2064.8)[f]	65	94:1:5
$PCy_2(p\text{-F-}C_6H_4)$	(162)[e]	(2061.3)[f]	86	98:1:1
PCy_2Ph	162	(2060.6)[f]	78	98:1:1
$PCy_2(p\text{-anisyl})$	(162)[e]	(2059.7)[f]	87	98:1:1
PCy_3	170	2056.4	19	>98:1:1
$P(o\text{-tolyl})_3$	194	2066.6	0	–
$P(o\text{-anisyl})_3$	(>194)[e]	2058.3	84[g]	52:20:28

[a] Ref. [23]. [b] The stretching frequencies (ν_{CO}) of the terminal CO of $[Ni(CO)_3\mathbf{L}]$ in CH_2Cl_2. Ref. [23]. [c] Yields were determined by ^{1}H NMR analysis using 1,4-dioxane as an internal standard. [d] Determined by ^{1}H NMR spectroscopy. [e] Estimated values. [f] Calculated values using Tolman's equation. Ref. [23]. [g] Isolated yield.

To suppress byproduct formation and improve the yield of **5b**, we aimed to accelerate the desired nickel-catalyzed ASR process. Screening of reaction conditions revealed three reaction parameters to be important for high yield of the desired product. First, the initial substrate concentration should be as high as 1 M (previously 0.2 M). Second, a combination of PCy_2Ph and $P(OPh)_3$ is necessary. $P(OPh)_3$ is envisioned to accelerate reductive elimination by reducing the electron density of the nickel center, as has been observed previously in the nickel–N-heterocyclic carbene-catalyzed coupling of alkenes and aldehydes.[8c] Third, carbonate **1a** must be mixed with the nickel complex prior to the addition of alkene. We have observed that $[Ni\mathbf{L}_2(\eta^2\text{-1-octene})]$ (**L** = PCy_2Ph) complex **12**,[30] generated by mixing $[Ni(cod)_2]$, PCy_2Ph, and 1-octene, is slowly converted (over 3 h), upon addition of **1a**, into an allyl–nickel complex **13**, whereas **13** can be readily formed (<10 min) in the absence of 1-octene (Scheme 3). When **1a** is mixed with the nickel complex prior to the addition of alkene, rapid generation of a key intermediate **13** should lead to the acceleration of the overall reaction process.[31]

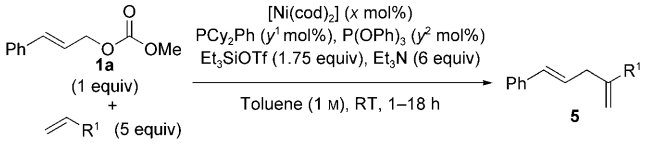


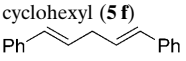
Scheme 3. Formation of allyl–nickel complex **13** in the presence or absence of 1-octene.

Under these conditions, many simple alkenes gave the coupling products **5** in good yield and with excellent selectivity, including the more sterically demanding vinylcyclohexane[32] (Table 5, entries 2–6). The opposite regioselectivity was observed in the case of styrene, with **14** being the sole coupling product (entry 7). A considerable amount of polystyrene was obtained in the reaction of styrene, probably due to Lewis acidic properties of the reaction conditions.

Several limitations to this method have been identified. Methyl acrylate and vinyl benzoate failed to react with **1a**, probably owing to the catalyst inhibition by an ester group of the substrates. A sterically demanding alpha-olefin, 3,3-dimethyl-1-butene, gave the desired product in low yield (<9%). Ethyl vinyl ether provided a complex reaction mixture that was difficult to purify. Cyclic internal alkenes, cyclopentene and cyclohexene, also gave a complex reaction mixture and the coupling products were isolated in low yields. The ASR reaction of vinylbromide with **1a** did not provide any of the desired product.

Table 5. Nickel-catalyzed allylic substitution of alkenes.



Entry	x	y^1	y^2	R^1 (product)	Yield [%][a]
1[b]	10	20	0	Me (**5a**)	77 (71)[c]
2	10	10	10	nC_6H_{13} (**5b**)	79
3	20	20	20	CH_2OSiEt_3 (**5c**)	73
4	10	10	10	$(CH_2)_2OTBS$ (**5d**)	83[d]
5	20	20	20	CH_2CHMe_2 (**5e**)	87
6[e]	20	40	0	cyclohexyl (**5f**)	64[f]
7	20	40	0	 **14**	25

[a] Isolated yield; *E*/*Z* selectivity >98:2 in all cases. [b] Propylene pressure 1 atm (balloon); toluene (0.2 M). [c] 5 mol% $[Ni(cod)_2]$, 10 mol% PCy_2Ph. [d] Yield of free alcohol after treatment with 1 N HCl. [e] Et_3SiOTf added over 4 h. [f] Yield includes trace amounts of regioisomers (total <8%).

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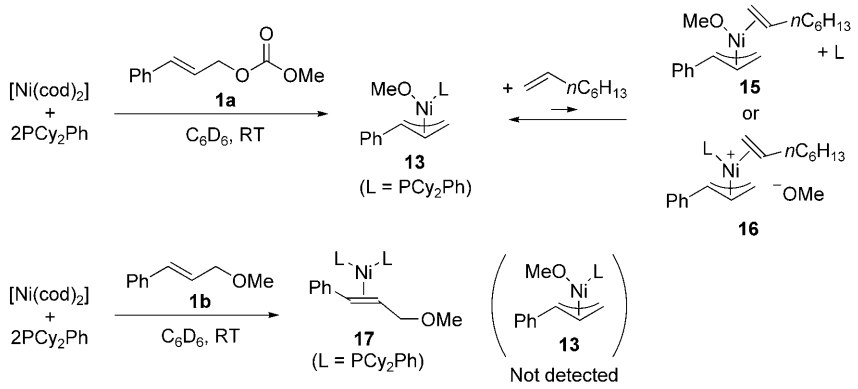
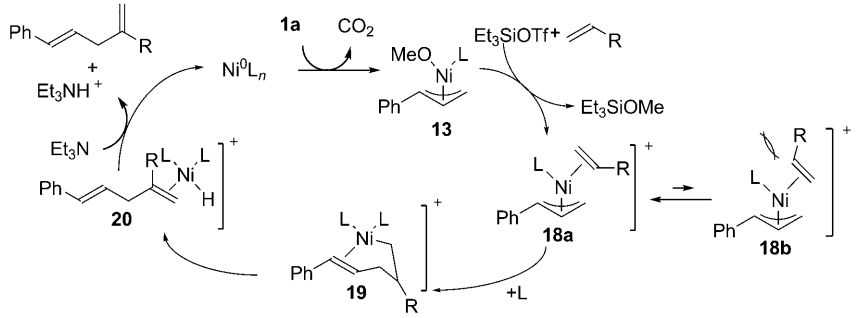
Reaction Mechanism of Nickel-Catalyzed Allylic Substitution of Simple Olefins

Nickel-catalyzed ASR of simple olefins requires Et_3SiOTf, and to determine the role of Et_3SiOTf, the oxidative addition step was studied by NMR spectroscopy (Scheme 4). When cinnamyl methyl carbonate (**1a**) was treated with a preformed nickel complex, oxidative addition occurred rapidly at room temperature without Et_3SiOTf to afford allyl–nickel complex **13**.[33] It is notable that **13** remained intact after addition of an excess amount of 1-octene and that the expected olefin complexes **15** or **16** were not observed. These data suggest that Et_3SiOTf-mediated anion exchange is required for 1-octene to coordinate to the nickel center and react with an allyl ligand. The necessary cationic property of nickel for subsequent olefin coordination has also been suggested by other groups.[34] On the other hand, mixing cinnamyl methyl ether (**1b**) with the nickel complex did not lead to oxidative addition, but simply resulted in formation of an olefin-nickel complex **17**.[35] Allyl-nickel complex **13** was not detected. Thus, in the case of the nickel-catalyzed ASR of alkenes by allylic alcohol derivatives bearing poor leaving groups such as OMe and $OSiMe_3$, Et_3SiOTf was found to be required for oxidative addition to take place.



Scheme 4. NMR spectroscopy study for the oxidative addition event of nickel-catalyzed ASR.

The proposed reaction mechanism is summarized in Scheme 5, in which **1a** is used as a representative allylic alcohol derivative. As mentioned above, allyl–nickel complex **13** is generated without assistance of Et_3SiOTf. The Ni–O bond of **13** is activated upon addition of Et_3SiOTf, thereby forming cationic allyl–nickel complex **18**. Subsequent migratory insertion (C–C bond-forming step) and coordination of another phosphine ligand afford **19**. Regioselectivity is determined in this olefin migration step. As mentioned above in the previous section, the bulkier phosphine ligands provided higher selectivity for the 1,1-disubsituted olefin. This observation can be explained by the supposition that as the steric bulkiness of the phosphine ligand becomes larger, allyl–nickel complex **18a** would be more favorable than **18b**. Although it is still unclear whether olefin migration requires coordination of another phosphine ligand, computational studies of the migration of an olefin ligand to an allyl ligand of a nickel or palladium complex have been reported.[34] Those studies suggest that the olefin migration step is thermoneutral or slightly uphill energetically and that concomitant coordination of a ligand to the resultant unsaturated metal center after olefin migration makes this process significantly favorable. β-Hydride elimination and subsequent reductive elimination provide the 1,4-diene product and regenerate the catalyst.

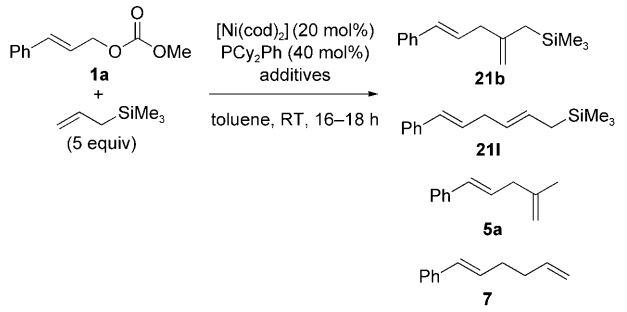


Scheme 5. Proposed mechanism of nickel-catalyzed allylic substitution of olefins (L = organophosphine; triflates (TfO^-) omitted for clarity).

Applications of Nickel-Catalyzed ASRNickel-Catalyzed Allylic Substitution of Allyltrimethylsilane

Allyl metal reagents such as allyl stannanes, silanes, and boronates are widely used for the introduction of a C_3 unit and are much stronger nucleophiles than simple alkenes.[36] Moreover, the fact that the attack of an electrophile on an allyl metal reagent takes place predictably at the terminal position of the double bond (distal from metal) makes allylation using an allyl metal reagent important in synthesis. Several allyl–allyl couplings between allylic alcohol derivatives and allyl metal reagents in the presence of various catalysts, providing 1,5-dienes exclusively, have been reported so far.[37]

With the intention of observing which position of the double bond is attacked in the nickel-catalyzed ASR of the allyl metal reagent, a reaction of **1a** and allyltrimethylsilane under the optimal reaction conditions was conducted (Scheme 6). The reaction proceeded smoothly to afford a mixture of products. It is note-

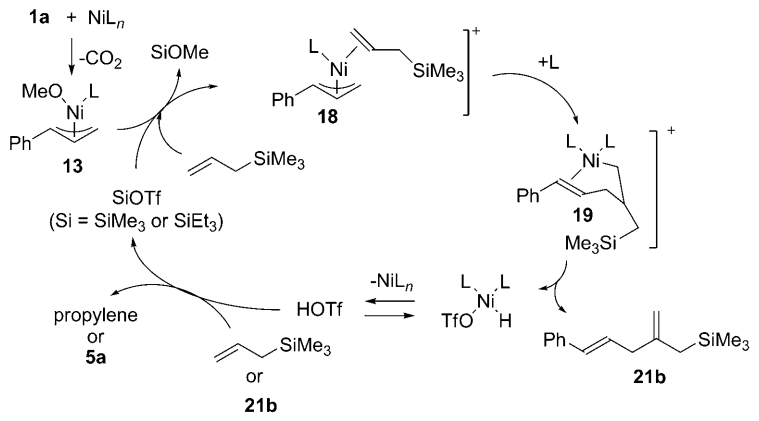


Et_3SiOTf (1.75 equiv), Et_3N (6 equiv): 77% yield (**21b**/**5a**/**21l**/**7** = 34:48:9:9)
Et_3SiOTf (20 mol%), No Et_3N: 82% yield (**21b**/**5a**/**21l**/**7** = 46:43:5:6)

Scheme 6. Nickel-catalyzed ASR of allyltrimethylsilane.

worthy that in this nickel-catalyzed reaction, the 1,1-disubstituted olefins **21b** and **5a**, generated through reaction at the internal position of the double bond, were the major products, overcoming the intrinsic nature of allyltrimethylsilane that generally affords linear 1,5-dienes (such as **7**). More surprisingly, the same level of yield and selectivity was observed in the presence of a catalytic amount of Et_3SiOTf (20 mol%) and no triethylamine. No reaction proceeded in the absence of Et_3SiOTf.

Although the isolation of a considerable amount of undesired protodesilylated product **5a** was a matter of concern, the catalytic turnover of silyl triflate is interesting from a mechanistic viewpoint. The proposed mechanism of the nickel-catalyzed ASR of allyltrimethylsilane using a catalytic amount of Et_3SiOTf is illustrated in Scheme 7. Given the fact that 1,1-disubstituted olefins **21b** and **5a** are the major products, the reaction pathways prior to the selectivity-determining step (migratory insertion from **18** to **19**) are thought to be similar to those described in Scheme 5. β-Hydride elimination from intermediate **19** provides 1,4-diene **21b** and $HNiL_2OTf$. A possible explanation of the fact that triethylamine is not required in this reaction would be that allyltrimethylsilane or silane **21b** function as acid scavengers, thereby trapping the HOTf liberated from $HNiL_2OTf$ (or more directly from $HNiL_2OTf$) to regenerate both silyl triflate and the nickel(0) species. In this transformation, allyltrimethylsilane and silane **21b** are converted into propylene and diene **5a**, respectively.[38]



Scheme 7. Proposed mechanism of nickel-catalyzed allylic substitution of allyltrimethylsilane (L = organophosphine; triflates (TfO^-) omitted for clarity).

Nickel-Catalyzed Reactions of Simple Alkenes with Vinyl Epoxide or Vinyltetrahydrofuran Derivatives

In addition to allylic alcohol derivatives, vinyl epoxide is also known to undergo oxidative addition with palladium(0) to afford allyl–palladium species, which then can be used as key intermediates for catalytic C–C bond-forming processes.[39] We envisioned that vinyl epoxide would react with a nickel(0)–phosphine complex to provide an allyl–nickel complex analogously to palladium chemistry,[40] and that the resultant allyl–nickel complex could be involved in the nickel-catalyzed ASR process of simple alkenes.

As expected, the nickel-catalyzed reaction of ethylene with butadiene monooxide proceeded in the presence of Et_3SiOTf in high yield, but the products were a mixture of linear adduct **22a** and branched adduct **23a** [Scheme 8, Eq. (7)]. Similar selectivity was also observed when PCy_2Ph was used instead of P(*o*-anisyl)$_3$. This anomalous low linear-to-branched selectivity, however, was observed only in the case of ethylene. A reaction of 1-octene with butadiene monooxide provided the corresponding linear adduct **24** exclusively [Scheme 8, Eq. (8)].

It is proposed that allyl–nickel complex **25** or its dimer or oligomer is generated in the oxidative addition of nickel(0) into butadiene monooxide (Scheme 9). Et_3SiOTf readily reacts with this nickel species to form cationic nickel complex **26** bearing triflate as a counter anion. Allyl–nickel complex **26a** resembles the nickel-containing species **18a** (Scheme 5), proposed as the intermediate that leads to linear products in the nickel-catalyzed ASR. Indeed, this pathway was predominant when 1-octene was employed with butadiene monooxide. However, when ethylene was used as a substrate, **26b** appears to comparably contribute to the product formation, thus resulting in branched adduct **23a**.

To probe the origin of the anomalous low selectivity in the reaction of ethylene with butadiene monooxide, allylic carbonate **1m** was employed as a starting material [Scheme 10, Eq. (9)]. A reaction of **1m** with ethylene proceeded to give a mixture of **22a** and **23a** with 60:40 selectivity, identical to that observed in a reaction of butadiene monooxide and ethylene. It is likely that a mixture of the intermediates **26a** and **26b** is generated for both butadiene monooxide and **1m**, which leads to low selectivity. It

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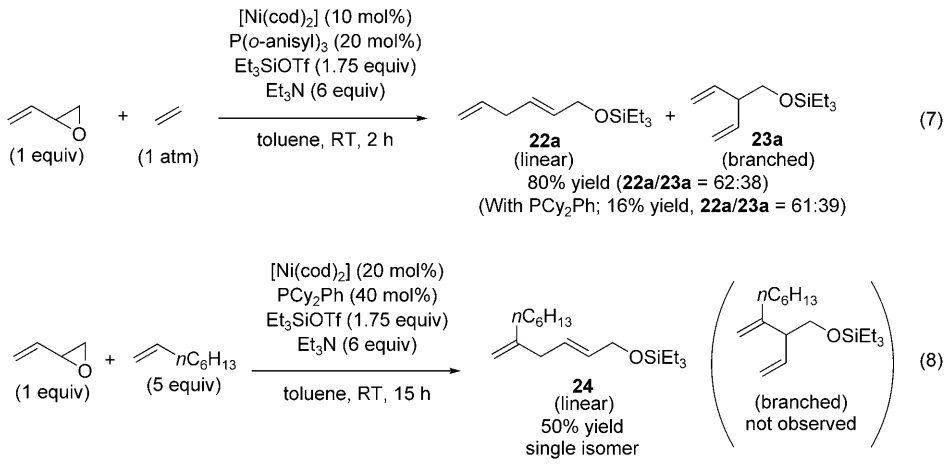
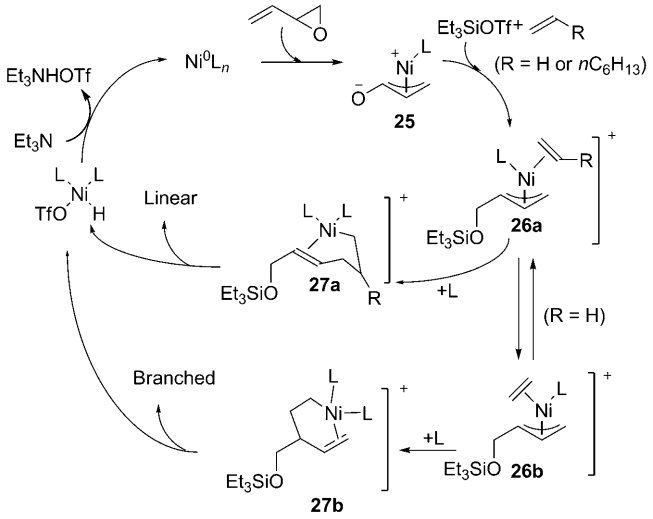


Scheme 8. Nickel-catalyzed reactions of alkenes with butadiene monooxide.



Scheme 9. Proposed mechanism of nickel-catalyzed reactions of alkenes with butadiene monooxide (L = organophosphine; triflates omitted for clarity).

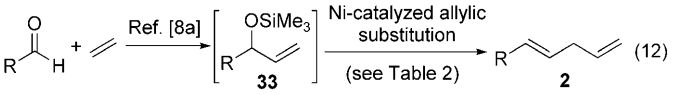
should be noted that allylic alcohol derivatives **1f** (C_1-homologue of **1m**), **1g**, and **1o** all gave linear products with high selectivity [Eq. (11)]. A reaction of **1m** with 1-octene gave linear product **24** exclusively [Scheme 10, Eq. (10)].

The observation that substrate **1n** bearing a sterically demanding triisopropylsilyl group on oxygen also provided low linear-to-branched selectivity (Scheme 10) rules out the possibility that coordination of an ethereal oxygen atom to the nickel metal center is causing the anomalous low selectivity. Alternatively, it is possible that the ethereal oxygen atom serves as an electron-withdrawing group to electronically dictate the regioselectivity of the reaction. The 3-position of the allyl ligand is more electrophilic in nature, and migratory insertion of ethylene from **28b** becomes an operative pathway (Scheme 11). On the other hand, in the case of 1-octene, the reaction from **29b** is still inhibited due to the steric bulk of 1-octene. As a result, in that case, linear product **24** is exclusively obtained (via **29a**). This rationalization is controversial because the hydroxy group was reported to be a strong directing group for formation of the new C–C bond distal to the hydroxy group in palladium-catalyzed ASR leading to regioselective linear product formation.[41]

Similarly, a reaction of 2-vinyltetrahydrofuran derivative **30** with ethylene was conducted (Scheme 12). Although a considerable amount of β-hydride elimination byproduct **32** was isolated, the desired product **31** was obtained in moderate yield.

Nickel-Catalyzed Reactions of Ethylene with Aldehydes, Leading to 1,4-Dienes

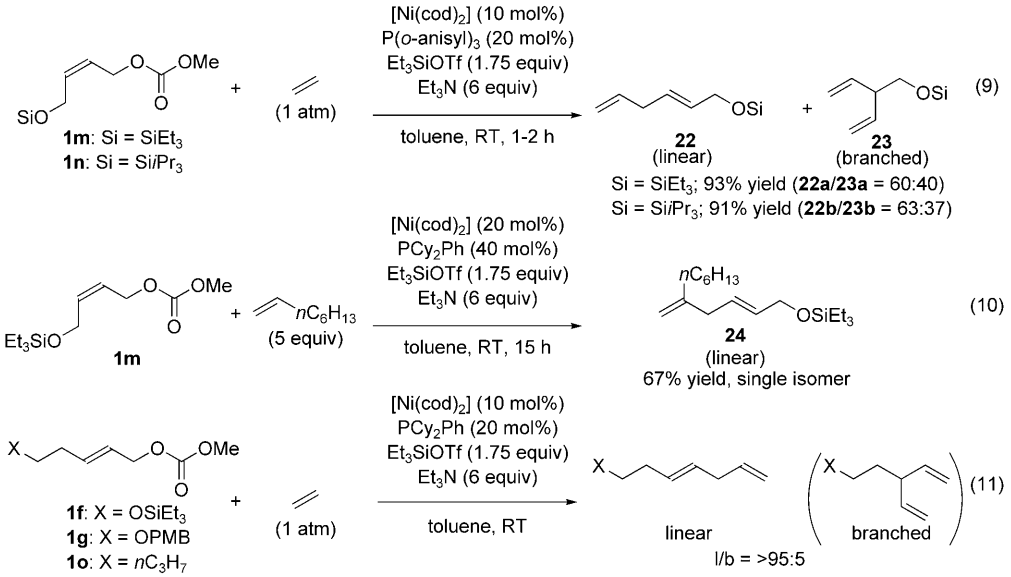
We previously reported the nickel-catalyzed intermolecular three-component coupling of aldehydes, silyl triflates, and alpha-olefins to provide silyl ethers of allylic alcohols **33**.[8a,c] Given that allyl trimethylsilyl ethers can be accommodated in the nickel-catalyzed ASR of ethylene (Table 2), we envisioned a one-step conversion of an aldehyde into a 1,4-diene [Eq. (12)].



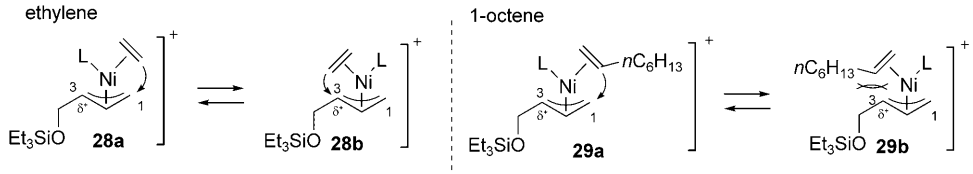
Unfortunately, the reaction of benzaldehyde with ethylene at room temperature (Scheme 13) provided the desired 1,4-diene **2a** in low yield (4%), along with a considerable amount of initial coupling product **33** (63% yield). The low conversion of **33** suggested that the second reaction was sluggish, probably owing to the steric bulkiness of the R group. Thus, the less sterically demanding cinnamyl aldehyde was chosen as a substrate. Gratifyingly, the corresponding 1,4-diene product **2b** was obtained in good yield. Despite the limited substrate scope, this reaction is a useful method that provides easy access to 1,4-dienes from aldehydes.

Nickel-Catalyzed Reactions of Ethylene with Aromatic Aldehyde-Derived Dimethyl Acetals

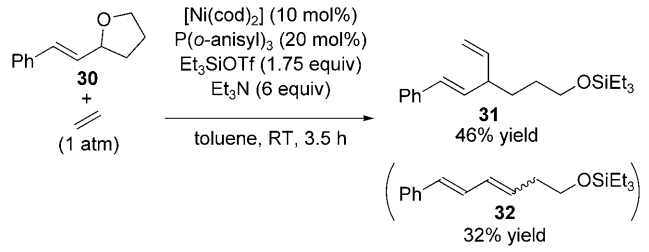
As stated above, the nickel-catalyzed reaction of ethylene with aromatic aldehydes failed to provide a 1,4-diene product due to the steric bulkiness of the initially formed product, allyl trimethylsilyl ether **33**. We then postulated that dimethyl acetals may react with ethylene and generate allyl



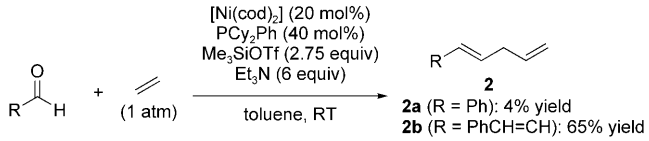
Scheme 10. Nickel-catalyzed ASR of alkenes with a methyl carbonate derived from 2-butene-1,4-diol.



Scheme 11. Olefin migration to allyl ligand with CH_2OSiEt_3 substituent (left: ethylene, right: 1-octene).



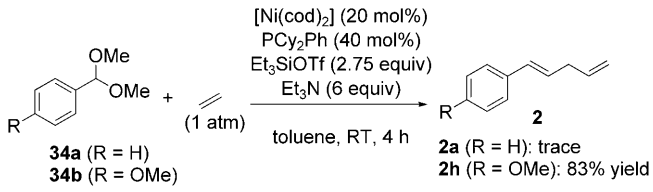
Scheme 12. Nickel-catalyzed reaction of ethylene with 2-vinyltetrahydrofuran **30**.



Scheme 13. Nickel-catalyzed reactions of ethylene with aldehydes, leading to 1,4-dienes.

methyl ether **39**. It was assumed that sterically less hindered **39** thus formed would further react with ethylene in the presence of Et_3SiOTf and nickel catalyst, thereby affording the desired 1,4-diene **2**.

Our first trial using benzaldehyde dimethyl acetal (**34a**) failed to afford any desired 1,4-diene **2a** or intermediate **39** (Scheme 14). At elevated temperature (60 °C), the desired product **2a** was observed, but a considerable amount of 1,3-diene **3a** was obtained. To our delight, electron rich *para*-anisaldehyde dimethyl acetal (**34b**) was found to be a superior substrate; the desired reaction proceeded at room temperature to afford 1,4-diene **2h** in 83% yield.



Scheme 14. Nickel-catalyzed reactions of ethylene with aromatic aldehyde-derived dimethyl acetals.

It is presumed that the first step of this reaction is activation of **35** by Et_3SiOTf then oxidative addition by the nickel(0)–phosphine complex to afford **36** (Scheme 15). Stabilization of the intermediate oxonium cation may explain why the electron-rich aromatic rings perform better in this reaction. There may be an equilibrium between the η^1-benzyl– and η^3-benzyl–nickel complex (**36** and **37**), the latter of which is similar to the allyl–nickel intermediate **18** in the nickel-catalyzed ASR. Migratory insertion then occurs at the benzyl position followed by β-hydride elimination, thus providing the initial coupling product **39**. Allyl methyl ether **39** is a good substrate for the subsequent nickel-catalyzed ASR of ethylene (cf. Table 2) and 1,4-diene **2h** is formed by means of the pathway proposed in Scheme 5.

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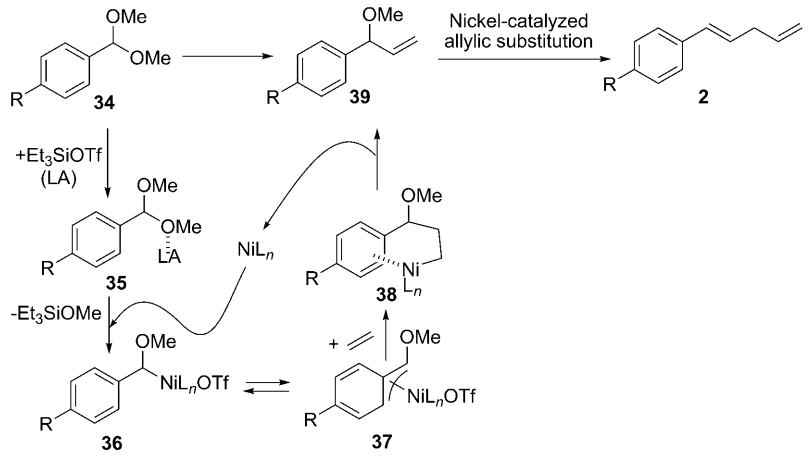

Scheme 15. Proposed mechanism for nickel-catalyzed reaction of ethylene with aromatic aldehyde dimethyl acetal **34**.

Conclusion

Herein, we have described the nickel-catalyzed allylic substitution reaction of simple alkenes for the formation of 1,4-dienes. The key for the reaction was the use of the appropriate nickel–phosphine complex and a stoichiometric amount of silyl triflate. Allylic alcohol derivatives, bearing a variety of leaving groups, can be coupled with a wide range of simple alkenes, which include gaseous ethylene and propylene. Reactions of 1-alkyl-substituted alkenes consistently provided 1,1-disubstituted alkenes with high selectivity. Silyl triflate is proposed to activate the Ni−O bond, generating a cationic allyl–nickel species poised for the subsequent migratory insertion event. In some cases, 1,3-dienes were also obtained as an inseparable byproduct. Therefore, a method utilizing TCNE to selectively trap (*E*)-1,3-dienes has been developed, whereby a convenient gram-scale synthesis of pure 1,4-diene was possible.

Nickel-catalyzed allylic substitution of allyltrimethylsilane was also developed, in which a catalytic amount of Et_3SiOTf promoted the reaction. Butadiene monooxide and 2-vinyltetrahydrofuran also performed well as a substrate, thereby generating the desired 1,4-dienes. Finally, the nickel-catalyzed allylic substitution technique was extended to novel types of transformations, namely, conversion of aldehydes and dimethyl acetals into 1,4-dienes. Further exploration into new methods utilizing simple alkenes is ongoing in our group.

Experimental Section

General Information

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of argon with rigorous exclusion of moisture from reagents and glassware. Toluene, dichloromethane, tetrahydrofuran, triethylamine, and diethyl ether were obtained from a solvent purification system (SG Water). Bis(cyclooctadienyl)nickel(0) ([Ni(cod)$_2$]) and phosphine ligands were purchased from Strem Chemicals, Inc. or Aldrich, stored under a nitrogen atmosphere and used without further purification. Ethylene and propylene were purchased from BOC Gases and Aldrich, respectively, and used as received. 1-Octene, vinylcyclohexane, and styrene were distilled from CaH_2 prior to use. All other reagents and solvents were used as obtained, without further purification. Analytical and preparative thin-layer chromatography were performed using EM Science silica gel 60 F254 plates. The developed chromatogram was visualized by a UV lamp or stained using one of the following: aqueous potassium permanganate ($KMnO_4$) and ethanolic phosphomolybdic acid (PMA). Liquid chromatography was performed by using a forced flow (flash chromatography) of the indicated solvent system on silica gel (230–400 mesh).

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300 MHz spectrometer, a Bruker AVANCE 400 MHz spectrometer, or Varian Inova 500 MHz spectrometers in $CDCl_3$, unless otherwise noted. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of tetramethylsilane in $CDCl_3$ (δ = 0.00 ppm) or residual benzene in C_6D_6 (δ = 7.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad), coupling constant, and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (δ = 77.00 ppm) or C_6D_6 (δ = 128.00 ppm). IR spectra were recorded on a Perkin–Elmer 2000 FTIR. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Fourier Transform Mass Spectrometer by Ms. Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility. GC–MS spectra were obtained on an Agilent 5973N gas chromatograph/mass spectrometer and the Restek Rtx-1 GC column (30 m × 250 μm × 1 μm) in the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility.

General Procedure for the Nickel-Catalyzed ASR Using Ethylene

A test tube (borosilicate glass, 16 × 100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol %) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol %) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15–30 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), allylalcohol derivative (0.5 mmol, 1 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 15–90 min. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and a certain amount of CH_3CN (10–20 mg) or $(PhCH_2)_2O$ (15–20 mg) as an internal standard was added to the residue. The mixture was completely dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The product yield was determined by referring to the methyl protons of CH_3CN or methylene protons of $(PhCH_2)_2O$.

General Procedure for Nickel-Catalyzed ASR Using Ethylene

A test tube (borosilicate glass, 16 × 100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol %) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol %) were added to the test tube, which was sealed with a septum; the test tube was taken out of the

glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15–30 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), allylalcohol derivative (0.5 mmol, 1 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 20–200 min. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1 v/v). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography or preparative thin-layer chromatography. The complete results are summarized in the Supporting Information.

*(E)-Penta-1,4-dienylbenzene (**2a**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.36 (m, 5H), 6.41 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 6.7, 15.9 Hz, 1H), 5.90 (dtt, J = 6.4, 10.1, 17.0 Hz, 1H), 5.11 (dq, J = 1.9, 17.1 Hz, 1H), 5.06 (dq, J = 1.4, 10.1 Hz, 1H), 2.96 ppm (dt, J = 1.5, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.5, 136.4, 130.8, 128.5, 128.1, 127.0, 126.0, 115.6, 37.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3080, 3060, 3026, 2978, 2891, 1944, 1637, 1599, 1495, 1448, 1429, 1305, 992, 965, 914, 742, 692 cm^{-1}.

*(1E)-Penta-1,3-dienylbenzene (**3a**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = distinguishable peaks are shown. (1*E*,3*E*)-isomer: δ = 6.74 (dd, J = 10.5, 15.7 Hz, 1H), 1.82 ppm (dd, J = 1.1, 6.8 Hz, 3H); (1*E*,3*Z*)-isomer: δ = 1.86 ppm (dd, J = 1.7, 7.2 Hz, 3H).

*(1E)-Hepta-1,3,6-trienylbenzene (**2b**)*

^{1}H NMR (500 MHz, $CDCl_3$): (1*E*,3*E*)-isomer: δ = 7.16–7.42 (m, 5H), 6.76 (dd, J = 10.5, 15.7 Hz, 1H), 6.46 (d, J = 15.7 Hz, 1H), 6.22 (dd, J = 10.5, 15.2 Hz, 1H), 5.77–5.91 (m, 2H), 5.07 (dq, J = 1.6, 17.2 Hz, 1H), 5.02–5.06 (m, 1H), 2.89 ppm (dt, J = 1.3, 6.7 Hz, 2H); (1*E*,3*Z*)-isomer: distinguishable peaks are shown; δ = 7.04 (ddd, J = 1.2, 11.1, 15.6 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 5.10 (dq, J = 1.8, 17.1 Hz, 1H), 5.53 ppm (dt, J = 7.7, 10.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): (1*E*,3*E*)-isomer: δ = 137.5, 136.3, 132.6, 131.5, 130.7, 129.0, 128.5, 127.2, 126.2, 115.6, 36.8; (1*E*,3*Z*)-isomer: δ = 137.4, 136.3, 132.7, 129.7, 129.4, 128.5, 127.5, 126.3, 124.0, 115.3, 32.1 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3079, 3060, 3023, 2910, 1944, 1844, 1680, 1637, 1596, 1495, 1448, 1428, 1295, 988, 913, 746, 691 cm^{-1}; HRMS-DART: m/z calcd for $C_{13}H_{15}$: 171.1168; found: 171.1171 $[M+H]^+$.

*Hepta-1,3,5-trienylbenzene (**3b**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 1.79 ppm (dd, J = 1.5, 6.8 Hz, 3H).

*tert-Butyl(hepta-3,6-dienyloxy)dimethylsilane (**2c**-linear)*

^{1}H NMR (500 MHz, $CDCl_3$): (*E*)-isomer: δ = 5.82 (ddt, J = 6.4, 10.4, 17.0 Hz, 1H), 5.40–5.55 (m, 2H), 5.02 (dq, J = 1.7, 17.1 Hz, 1H), 4.98 (dd, J = 1.3, 10.1 Hz, 1H), 3.62 (t, J = 6.9 Hz, 2H), 2.75 (t, J = 6.1 Hz, 2H), 2.23 (q, J = 6.7 Hz, 2H), 0.89 (s, 9H), 0.05 ppm (s, 6H); (*Z*)-isomer: distinguishable peaks are shown; δ = 2.81 ppm (t, J = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E*)-isomer: δ = 137.1, 129.8, 127.8, 114.9, 63.2, 36.8, 36.3, 25.9, 18.4, −5.2 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 2929, 2858, 1472, 1255, 1102, 968, 912, 836, 775 cm^{-1}; HRMS-DART: m/z calcd for $C_{13}H_{27}OSi$: 227.1826; found: 227.1829 $[M+H]^+$.

*tert-Butyldimethyl(3-vinylpent-4-enyloxy)silane (**2c**-branched)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 5.73 (ddd, J = 7.5, 10.5, 17.4 Hz, 2H), 2.89 ppm (quint, J = 7.3 Hz, 1H).

*1-[(Hepta-3,6-dienyloxy)methyl]-4-methoxybenzene (**2d**-linear)*

^{1}H NMR (500 MHz, $CDCl_3$): (*E*)-isomer: δ = 7.26 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.81 (ddt, J = 6.4, 10.1, 17.2 Hz, 1H), 5.42–5.55 (m, 2H), 4.96–5.05 (m, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.46 (t, J = 6.9 Hz, 2H), 2.75 (t, J = 5.7 Hz, 2H), 2.32 ppm (dq, J = 0.7, 6.9 Hz, 2H); (*Z*)-isomer: distinguishable peaks are shown; δ = 2.81 ppm (t, J = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E*)-isomer: δ = 159.0, 137.0, 130.5, 129.7, 129.2, 127.6, 114.9, 113.7, 72.4, 69.7, 55.2, 36.7, 33.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3076, 3000, 2934, 2906, 2854, 1637, 1613, 1586, 1513, 1464, 1441, 1361, 1302, 1248, 1208, 1172, 1098, 1037, 993, 971, 913, 821, 756 cm^{-1}; HRMS-DART: m/z calcd for $C_{15}H_{21}O_2$: 233.1536; found: 233.1534 $[M+H]^+$.

*1-Methoxy-4-[(3-vinylpent-4-enyloxy)methyl]benzene (**2d**-branched)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 5.71 (ddd, J = 7.5, 10.4, 17.2 Hz, 2H), 2.90 ppm (quint, J = 7.4 Hz, 1H).

*Hexa-2,5-dien-2-ylbenzene (**2e**)*

^{1}H NMR (500 MHz, $CDCl_3$): (*E*)-isomer: δ = 7.38–7.41 (m, 2H), 7.28–7.33 (m, 2H), 7.17–7.26 (m, 1H), 5.89 (ddt, J = 10.1, 17.1, 6.2 Hz, 1H), 5.80 (tq, J = 7.3, 1.4 Hz, 1H), 5.10 (dq, J = 17.1, 1.8 Hz, 1H), 5.02 (dq, J = 10.1, 1.9 Hz, 1H), 2.97 (t, J = 7.0 Hz, 2H), 2.04 ppm (d, J = 1.4 Hz, 3H); (*Z*)-isomer: distinguishable peaks are shown; δ = 5.49 (tq, J = 7.6, 1.5 Hz, 1H), 2.72 ppm (ddq, J = 6.1, 6.1, 1.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E*)-isomer: δ = 143.7, 136.6, 135.9, 128.1, 126.6, 125.6, 125.2, 114.8, 33.0, 15.8 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3079, 3058, 3031, 2977, 2922, 1637, 1598, 1493, 1444, 1379, 1026, 993, 910, 756, 695 cm^{-1}; HRMS-EI: m/z calcd for $C_{12}H_{14}$: 158.1090; found: 158.1094 $[M]^+$.

*(2E)-Hexa-2,4-dien-2-ylbenzene (**3c**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 1.86 ppm (d, J = 6.7 Hz, 3H).

*(E)-Hexa-2,5-dien-3-ylbenzene (**3d**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 3.26 (d, J = 5.9 Hz, 2H), 1.79 ppm (d, J = 6.9 Hz, 3H).

*(2-Methylpenta-1,4-dienyl)benzene (**2f**)*

^{1}H NMR (500 MHz, $CDCl_3$): (*E*)-isomer: δ = 7.27–7.33 (m, 2H), 7.21–7.26 (m, 2H), 7.16–7.20 (m, 1H), 6.30 (s, 1H), 5.88 (ddt, J = 10.1, 17.0, 6.9 Hz, 1H), 5.07–5.15 (m, 2H), 2.90 (d, J = 6.9 Hz, 2H), 1.85 ppm (d, J = 1.3 Hz, 3H); (*Z*)-isomer: distinguishable peaks are shown; δ = 6.39 (s, 1H), 2.96 (d, J = 6.2 Hz, 2H), 1.88 ppm (d, J = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): (*E*)-isomer: δ = 138.4, 137.2, 136.4, 128.8, 128.0, 125.9, 125.7, 116.3, 45.0, 17.8; (*Z*)-isomer: distinguishable peaks are shown; δ = 115.9, 37.2, 28.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3079, 3023, 2977, 2911, 1653, 1635, 1492, 1441, 1383, 1172, 1073, 993, 915, 830, 742, 698 cm^{-1}; HRMS-EI: m/z calcd for $C_{12}H_{14}$: 158.1090; found: 158.1092 $[M]^+$.

*(E)-(3-Methylpenta-1,4-dienyl)benzene (**2g**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.36 (m, 5H), 6.36 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 7.1, 16.0 Hz, 1H), 5.86 (ddd, J = 6.6, 10.3, 17.0 Hz, 1H), 5.07 (dt, J = 17.0, 1.5 Hz, 1H), 5.01 (dt, J = 10.3, 1.4 Hz, 1H), 2.97–3.07 (m, 1H), 1.19 ppm (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.4, 137.6, 134.2, 128.6, 128.4, 127.0, 126.0, 113.3, 40.6, 19.8 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 3060, 3026, 2966, 2927, 2869, 1635, 1599, 1495, 1448, 1411, 1369, 994, 965, 913, 747, 692 cm^{-1}; HRMS-EI: m/z calcd for $C_{12}H_{14}$: 158.1090; found: 158.1089 $[M]^+$.[43]

(*E*)-Buta-1,3-dienylbenzene (**3e**) was previously reported.

Gram-Scale ASR of Ethylene

A round-bottomed flask and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (68.8 mg, 0.25 mmol, 2.5 mol%) and P(*o*-anisyl)$_3$ (352 mg, 1 mmol, 10 mol%) were added to the flask, which was sealed with a septum; the flask was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (50 mL) under argon and stirred for 15 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (8.4 mL, 60 mmol, 6 equiv), cinnamyl methylcarbonate (10 mmol, 1 equiv), and Et_3SiOTf (4.0 mL, 17.5 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at

room temperature for 2 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1 v/v). The solvents were removed under reduced pressure and the crude mixture was dissolved in benzene (50 mL). Tetracyanoethylene (256 mg, 20 mol%) was added to the reaction mixture, and the reaction mixture was kept stirring for 30 min at room temperature. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography, to afford **2a** (1.18 g, >98% purity, 81% yield) along with **4** (134.8 mg, 5% yield). The inseparable impurity was (3*Z*)-**3a** (<2% yield).

*3-Methyl-6-phenylcyclohex-4-ene-1,1,2,2-tetracarbonitrile (**4**)*

M.p. 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.51 (m, 5H), 6.10 (ddd, J = 2.8, 3.6, 10.6 Hz, 1H), 6.00 (dt, J = 10.6, 2.1 Hz, 1H), 4.29 (q, J = 2.5 Hz, 1H), 3.28–3.37 (m, 1H), 1.73 ppm (d, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.8, 130.2, 129.8, 129.2, 128.6, 124.5, 111.6, 111.3, 110.0, 109.7, 46.6, 42.9, 42.8, 37.5, 17.8 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3036, 2098, 2255, 1495, 1455, 1393, 1379, 1219, 1169, 1115, 1031, 911, 823, 753, 735, 702 cm^{-1}; HRMS-DART: m/z calcd for $C_{17}H_{12}N_4$: 273.1135; found: 273.1130 $[M+H]^+$.

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with Propene

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol%) and the phosphine ligand (0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15 min at room temperature. The reaction mixture was purged with propene for 1 min to remove argon, taking care not to introduce oxygen. The propene atmosphere was maintained with a propene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 3.5 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure, and a certain amount of 1,4-dioxane was added to the mixture as an internal standard. The mixture was completely dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The product yield and selectivity were determined by reference to the methylene protons of 1,4-dioxane.

*(E)-(4-Methylpenta-1,4-dienyl)benzene (**5a**)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (27.4 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15 min at room temperature. The reaction mixture was purged with propene for 1 min to remove argon, taking care not to introduce oxygen. The propene atmosphere was maintained with a propene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 3.5 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **5a** (61.1 mg, 77% yield, >98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.38 (m, 2H), 7.25–7.31 (m, 2H), 7.15–7.22 (m, 1H), 6.34–6.44 (m, 1H), 6.16–6.26 (m, 1H), 4.79 (br s, 1H), 4.78 (br s, 1H), 2.89 (d, J = 7.0 Hz, 2H), 1.76 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.5, 137.6, 131.3, 128.5, 128.2, 127.0, 126.0, 111.0, 41.5, 22.5 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3080, 3026, 2970, 2935, 1646, 1495, 1448, 1373, 965, 889, 740, 691 cm^{-1}; HRMS-EI: m/z calcd for $C_{12}H_{14}$: 158.1090; found: 158.1096 $[M]^+$.

*(1E)-Hexa-1,4-dienylbenzene (**6**)*

(A mixture of (1*E*,4*E*) and (1*E*,4*Z*)-isomers): ^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 5.45–5.62 (m, 2H), 1.65–1.72 ppm (m, 3H).

*(E)-Hexa-1,5-dienylbenzene (**7**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 5.86 (ddt, J = 6.6, 10.2, 17.1 Hz, 1H), 5.06 (dq, J = 1.6, 17.1 Hz, 1H), 4.99 (ddt, J = 1.2, 2.0, 10.2 Hz, 1H), 2.31 (q, J = 6.8 Hz, 2H), 2.23 ppm (q, J = 6.7 Hz, 2H).

*(E)-(4-Methylenedec-1-enyl)benzene (**5b**)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and brought into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (13.7 mg, 0.05 mmol, 10 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperature. $P(OPh)_3$ (13.1 μL, 0.05 mmol, 10 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), 1-octene (393 μL, 2.5 mmol, 5 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 18 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford **5b** (90.4 mg, 79% yield, >98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.38 (m, 2H), 7.27–7.32 (m, 2H), 7.17–7.22 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.8, 7.1 Hz, 1H), 4.77–4.81 (m, 2H), 2.90 (d, J = 7.1 Hz, 2H), 2.05 (t, J = 7.6 Hz, 2H), 1.40–1.50 (m, 2H), 1.25–1.35 (m, 8H), 0.88 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.7, 137.6, 131.2, 128.5, 127.0, 126.0, 110.0, 39.9, 36.1, 31.8, 29.0, 27.6, 22.6, 14.1 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 3026, 2955, 2927, 2856, 1644, 1495, 1449, 965, 891, 739, 691 cm^{-1}; HRMS-EI: m/z calcd for $C_{17}H_{24}$: 228.1873; found: 228.1875 $[M]^+$.

*(E)-Triethyl(2-methylene-5-phenylpent-4-enyloxy)silane (**5c**)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (27.4 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at Rroom temperature. $P(OPh)_3$ (26.2 μL, 0.1 mmol, 20 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), allyloxytriethylsilane[44] (514 μL, 2.5 mmol, 5 equiv) and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 50 min. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford **5c** (104.8 mg, 73% yield, >98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.38 (m, 2H), 7.28–7.32 (m, 2H), 7.19–7.23 (m, 1H), 6.42 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.8, 7.1 Hz, 1H), 5.12 (s, 1H), 4.92 (s, 1H), 4.12 (s, 2H), 2.94 (d, J = 6.6 Hz, 2H), 0.97 (t, J = 8.0 Hz, 9H), 0.63 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.1, 137.5, 131.5, 128.5, 127.8, 127.0, 126.0, 110.1, 65.4, 36.4, 6.8, 4.4 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3026, 2955, 2910, 2876, 1238, 1111, 1078, 1007, 965, 900, 803, 741, 691 cm^{-1}; HRMS-ESI: m/z calcd for $C_{18}H_{29}OSi$: 311.1802; found: 311.1809 $[M+H]^+$.

*(E)-3-Methylene-6-phenylhex-5-en-1-ol (**5d**-alcohol form)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. [Ni(cod)$_2$] (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (13.7 mg, 0.05 mmol, 10 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glove-

box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperatre. $P(OPh)_3$ (13.1 μL, 0.05 mmol, 10 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), 3-buten-1-ol *tert*-butyldimethylsilyl ether[45] (573 μL, 2.5 mmol, 5 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 16 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford a mixture of **5d** and 3-buten-1-ol *tert*-butyldimethylsilyl ether, which were found to be inseparable from each other. The mixture was dissolved in MeOH (3 mL), and 12 N HCl aq. (ca. 100 mg) was added at room temperature. The mixture was stirred for 10 min at room temperature, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **5d**-alcohol form (78.0 mg, 83% yield in 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.38 (m, 2H), 7.27–7.32 (m, 2H), 7.18–7.23 (m, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 7.1 Hz, 1H), 4.97 (d, J = 1.4 Hz, 1H), 4.91 (s, 1H), 3.75 (t, J = 6.3 Hz, 2H), 2.94 (d, J = 7.0 Hz, 2H), 2.35 (t, J = 6.4 Hz, 2H), 1.55 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 137.3, 131.8, 128.5, 127.6, 127.1, 126.0, 113.0, 60.3, 39.6, 39.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3352, 3080, 3026, 2888, 1644, 1598, 1495, 1448, 1046, 967, 896, 741, 692 cm^{-1}; HRMS-ESI: m/z calcd for $C_{13}H_{16}ONa$: 211.1093; found: 211.1098 $[M+Na]^+$.

*(E)-(6-Methyl-4-methylenehept-1-enyl)benzene (**5e**)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (27.4 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperature. $P(OPh)_3$ (26.2 μL, 0.1 mmol, 20 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), 4-methyl-1-pentene (316 μL, 2.5 mmol, 5 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 21 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford **5e** (87.2 mg, 87% yield, >98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.38 (m, 2H), 7.27–7.31 (m, 2H), 7.17–7.22 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 7.1 Hz, 1H), 4.83 (d, J = 1.7 Hz, 1H), 4.77 (s, 1H), 2.88 (d, J = 7.1 Hz, 2H), 1.94 (d, J = 7.3 Hz, 2H), 1.76–1.85 (m, 1H), 0.89 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3, 137.6, 131.3, 128.5, 128.4, 127.0, 126.0, 111.5, 45.9, 39.5, 25.9, 22.5 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 3026, 2954, 2924, 2868, 1642, 1496, 1464, 1449, 1383, 1366, 966, 894, 741, 691 cm^{-1}; HRMS-Dart: m/z calcd for $C_{15}H_{19}$: 199.1481; found: 199.1486 $[M-H]^+$.

*(E)-(4-Cyclohexylpenta-1,4-dienyl)benzene (**5f**)*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperature. Triethylamine (418 μL, 3 mmol, 6 equiv) and vinylcyclohexane (342 μL, 2.5 mmol, 5 equiv) were added in the above order. Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) was then added over 4 h by using a syringe pump. The mixture was stirred at room temperature for another 12 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **5f** (72.4 mg, 64% yield). Inseparable regioisomers are included (<10% yield) in the reported yield. For more details, see the Supporting Information. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.38 (m, 2H), 7.27–7.31 (m, 2H), 7.17–7.22 (m, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.21 (dt, J = 15.8, 7.1 Hz, 1H), 4.80 (s, 1H), 4.76 (d, J = 1.5 Hz, 1H), 2.93 (d, J = 7.0 Hz, 2H), 1.10–1.93 ppm (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 137.7, 131.1, 128.9, 128.5, 126.9, 126.0, 108.4, 44.1, 38.6, 32.3, 26.7, 26.4 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 3025, 2925, 2851, 1639, 1495, 1448, 965, 887, 742, 691 cm^{-1}; HRMS-EI: m/z calcd for $C_{17}H_{22}$: 226.1716; found: 226.1711 $[M]^+$.

*(1E,4E)-1,5-Diphenylpenta-1,4-diene (**14**)[46]*

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperature. Triethylamine (418 μL, 3 mmol, 6 equiv), styrene (286 μL, 2.5 mmol, 5 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 18 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford **14** (27.7 mg, 25% yield).

Experimental Procedure for Ni-Catalyzed ASR of Allyltrimethylsilane Using a Catalytic Amount of Et_3SiOTf

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.1 mmol, 2 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was take out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at room temperature. Allyltrimethylsilane (397 μL, 2.5 mmol, 5 equiv) and Et_3SiOTf (22.6 μL, 0.1 mmol, 20 mol%) were added in the above order. The mixture was stirred at room temperature for 18 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford an inseparable mixture of **21b**, **5a**, **21l**, and **7** (80.4 mg, 82% yield; **21b**/**5a**/**21l**/**7** = 46:43:5:6).

*(E)-Trimethyl(2-methylene-5-phenylpent-4-enyl)silane (**21b**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.40 (m, 4H), 7.18–7.24 (m, 1H), 6.37–6.46 (m, 1H), 6.18–6.28 (m, 1H), 4.70 (d, J = 1.8 Hz, 1H), 4.61 (s, 1H), 2.87 (d, J = 6.9 Hz, 2H), 1.60 (s, 2H), 0.07 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.1, 137.6, 131.4, 128.5, 128.4, 127.0, 126.0, 108.4, 42.0, 26.7, −1.3 ppm; IR (NaCl plate, thin film): (a mixture of **21b**, **5a**, **21l**, and **7**): $\tilde{\nu}$ = 3081, 3026, 2954, 2895, 1942, 1872, 1632, 1599, 1578, 1495, 1448, 1422, 1247, 1155, 965, 851, 741, 692 cm^{-1}; HRMS-ESI: m/z: calcd for $C_{15}H_{22}SiNa$: 253.1383; found: 253.1381 $[M+Na]^+$.

*Trimethyl[(2E,5E)-6-phenylhexa-2,5-dienyl]silane (**21l**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; δ = 1.47 ppm (dd, J = 0.7, 8.0 Hz, 2H).

Experimental Procedure for the Nickel-Catalyzed Ring-Opening Reaction of Butadiene Monoxide by Ethylene

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (13.8 mg, 0.05 mmol, 10 mol%) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dis-

solved in toluene (2.5 mL) under argon and stirred for 15–30 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), butadiene monoxide (40.3 μL, 0.5 mmol, 1 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 2 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography, to afford a mixture of **22a** and **23a** (85.3 mg, 80% yield, **22a**/**23a** = 62:38).

*(E)-Triethyl(hexa-2,5-dienyloxy)silane (**22a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddt, J = 10.2, 16.9, 6.4 Hz, 1H), 5.55–5.73 (m, 2H), 4.97–5.07 (m, 2H), 2.79 (tq, J = 6.4, 1.4 Hz, 2H), 0.96 (t, J = 7.8 Hz, 9H), 0.61 ppm (q, J = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 130.2, 128.9, 115.3, 63.5, 36.3, 6.7, 4.5 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 2955, 2912, 2877, 1638, 1458, 1414, 1378, 1239, 1105, 1050, 1015, 971, 913, 810, 744, 668 cm^{-1}; HRMS-ESI: m/z calcd for $C_{12}H_{24}OSiNa$: 235.1489; found: 235.1491 $[M+Na]^+$.

*Triethyl(2-vinylbut-3-enyloxy)silane (**23a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75–5.88 (m, 2H), 5.10–5.12 (m, 2H), 5.08 (ddd, J = 1.1, 1.8, 5.4 Hz, 2H), 3.59 (d, J = 6.9 Hz, 2H), 2.93 (quint+t, J = 7.1, 1.2 Hz, 1H), 0.95 (t, J = 8.1 Hz, 9H), 0.59 ppm (q, J = 8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 115.9, 66.0, 50.4, 6.8, 4.4 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 2956, 2912, 2877, 1640, 1458, 1415, 1378, 1239, 1175, 1106, 1004, 915, 804, 744 cm^{-1}; HRMS-ESI: m/z calcd for $C_{12}H_{24}OSiNa$: 235.1489; found: 235.1492 $[M+Na]^+$.

Experimental Procedure for Nickel-Catalyzed Ring Opening Reaction of Butadiene Monoxide by 1-Octene

A test tube (borosilicate glass, 16 × 100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.10 mmol, 20 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at room temperature. Butadiene monoxide (40.3 μL, 0.5 mmol, 1 equiv) was added to the reaction mixture, and the mixture was stirred for 30 min. Triethylamine (418 μL, 3 mmol, 6 equiv), 1-octene (393 μL, 2.5 mmol, 5 equiv), and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 15 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography to afford **24** (77.9 mg, 53% yield).

*(E)-Triethyl(5-methyleneundec-2-enyloxy)silane (**24**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (dtt, J = 15.2, 1.3, 6.8 Hz, 1H), 5.60 (dtt, J = 15.2, 5.3, 1.2 Hz, 1H), 4.73 (d, J = 4.8 Hz, 1H), 4.14 (dq, J = 5.2, 1.2 Hz, 1H), 2.73 (d, J = 6.3 Hz, 2H), 2.00 (t, J = 7.4 Hz, 2H), 1.37–1.46 (m, 2H), 1.23–1.35 (m, 6H), 0.96 (t, J = 7.8 Hz, 9H), 0.88 (t, J = 7.1 Hz, 3H), 0.61 ppm (q, J = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 130.8, 129.1, 109.5, 63.5, 39.1, 36.0, 31.8, 29.0, 27.6, 22.6, 14.1, 6.8, 4.5 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3078, 2956, 2929, 2876, 1645, 1458, 1414, 1378, 1239, 1121, 1050, 1015, 971, 891, 810, 744, 671 cm^{-1}; HRMS-ESI: m/z calcd for $C_{18}H_{36}OSiNa$: 319.2428; found: 319.2423 $[M+Na]^+$.

*(E)-Triisopropyl(hexa-2,5-dienyloxy)silane (**22b**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.83 (ddt, J = 10.2, 17.1, 6.4 Hz, 1H), 5.70 (dtt, J = 15.3, 1.6, 6.5 Hz, 1H), 5.59 (dtt, J = 15.3, 1.4, 4.9 Hz, 1H), 5.04 (dq, J = 17.1, 1.7 Hz, 1H), 4.96–5.02 (m, 1H), 4.22 (dq, J = 4.9, 1.4 Hz, 2H), 2.80 (tq, J = 6.4, 1.4 Hz, 2H), 1.04–1.14 ppm (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.8, 130.5, 128.0, 115.2, 63.8, 36.3, 18.0, 12.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 2943, 2892, 2866, 1639, 1463, 1380, 1250, 1132, 1107, 1060, 1013, 994, 970, 914, 882, 800, 750, 682, 658 cm^{-1}; HRMS-ESI: m/z calcd for $C_{15}H_{30}OSiNa$: 277.1958; found: 277.1954 $[M+Na]^+$.

*Triisopropyl(2-vinylbut-3-enyloxy)silane (**23b**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.81–5.89 (m, 2H), 5.09–5.11 (m, 2H), 5.06–5.08 (m, 2H), 3.68 (d, J = 6.5 Hz, 2H), 2.91–2.96 (m, 1H), 1.02–1.10 ppm (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.2, 115.7, 66.6, 50.6, 18.0, 12.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 3081, 2943, 2894, 2866, 1836, 1640, 1464, 1413, 1383, 1247, 1113, 1069, 995, 916, 882, 789, 682, 659 cm^{-1}; HRMS-ESI: m/z calcd for $C_{15}H_{30}OSiNa$: 277.1958; found: 277.1956 $[M+Na]^+$.

Experimental Procedure for Nickel-Catalyzed Ring Opening Reaction of (E)-2-styryltetrahydrofuran by Ethylene

A test tube (borosilicate glass, 16 × 100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (13.8 mg, 0.05 mmol, 10 mol%) and P(o-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15–30 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), (*E*)-2-styryltetrahydrofuran (**30**; 84.6 μL, 0.5 mmol, 1 equiv; for its synthesis, see the Supporting Information) and Et_3SiOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in the above order. The mixture was stirred at room temperature for 3.5 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography, to afford a mixture (118.8 mg) of **31** (46% yield) and **32** (32% yield, E/Z = 82:18). To characterize **31**, the mixture thus obtained was treated with tetracyanoethylene (TCNE) in benzene for 30 min at room temperature to remove **32**.

*(E)-Triethyl(6-phenyl-4-vinylhex-5-enyloxy)silane (**31**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.42 (m, 2H), 7.26–7.31 (m, 2H), 7.16–7.22 (m, 1H), 6.37 (d, J = 15.9 Hz, 1H), 6.10 (dd, J = 7.8, 15.9 Hz, 1H), 5.79 (ddd, J = 7.3, 10.3, 17.3 Hz, 1H), 5.07 (d, J = 17.3 Hz, 1H), 5.03 (d, J = 10.3 Hz, 1H), 3.62 (t, J = 6.1 Hz, 1H), 2.86 (quint, J = 7.0 Hz, 1H), 1.51–1.62 (m, 4H), 0.95 (t, J = 7.9 Hz, 9H), 0.59 ppm (q, J = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2, 137.6, 133.0, 129.7, 128.4, 127.0, 126.0, 114.4, 62.8, 46.9, 30.9, 30.5, 6.8, 4.4 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$ = 2953, 2911, 2876, 1635, 1599, 1494, 1457, 1414, 1385, 1238, 1098, 1006, 965, 913, 799, 745, 693 cm^{-1}; HRMS-ESI: m/z calcd for $C_{20}H_{33}OSi$: 317.2295; found: 317.2289 $[M+H]^+$.

*Triethyl[(6E)-7-phenylhepta-4,6-dienyloxy]silane (**32**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; (*E*)-isomer: δ = 6.74 (dd, J = 10.4, 15.7 Hz, 1H), 6.45 (d, J = 15.7 Hz, 1H), 6.25 (dd, J = 10.4, 15.2 Hz, 1H), 3.68 (t, J = 6.9 Hz, 2H), 2.38 (q, J = 6.9 Hz, 2H), 0.97 (t, J = 7.2 Hz, 9H). (*Z*): 7.07 (ddd, J = 1.0, 11.1, 15.6 Hz, 1H), 6.53 (d, J = 15.6 Hz, 1H), 5.54 (dt, J = 10.8, 7.7 Hz, 1H), 3.69 (t, J = 7.0 Hz, 2H), 2.54 ppm (dq, J = 1.5, 7.2 Hz, 2H); HRMS-ESI: m/z calcd for $C_{18}H_{28}OSi$: 289.1988; found: 289.1989 $[M+H]^+$.

Experimental Procedure for Nickel-Catalyzed Reaction of Ethylene with Cinnamyl Aldehyde

A test tube (borosilicate glass, 16 × 100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.10 mmol, 20 mol%) and P(o-anisyl)$_3$ (70.5 mg, 0.20 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL,

3 mmol, 6 equiv), cinnamyl aldehyde (62.9 μL, 0.5 mmol, 1 equiv), and Me_3SiOTf (249 μL, 1.38 mmol, 2.75 equiv) were added in the above order. The mixture was stirred at room temperature for 23 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography to afford **2b** (65% yield).

Experimental Procedure for Nickel-Catalyzed Reaction of Ethylene with para-Anisaldehyde Dimethylacetal

A test tube (borosilicate glass, 16×100 mm) and a stirrer bar were oven-dried and put into a glovebox. $[Ni(cod)_2]$ (27.5 mg, 0.10 mmol, 20 mol%) and P(*o*-anisyl)$_3$ (70.5 mg, 0.20 mmol, 40 mol%) were added to the test tube, which was sealed with a septum; the test tube was taken out of the glovebox and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15 min at room temperature. The reaction mixture was purged with ethylene for 1 min to remove argon, taking care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), *p*-anisaldehyde dimethylacetal (**34b**, 85.1 μL, 0.5 mmol, 1 equiv), and Et_3SiOTf (311 μL, 1.38 mmol, 2.75 equiv) were added in the above order. The mixture was stirred at room temperature for 4 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane/EtOAc (1:1). The solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography to afford a mixture of **2h** (83% yield) and 1-methoxy-4-(penta-1,3-dienyl)benzene (**3f**, 12% yield).

*(E)-1-Methoxy-4-(penta-1,4-dienyl)benzene (**2h**)*

^{1}H NMR (500 MHz, $CDCl_3$): δ=7.27–7.30 (m, 2H), 6.82–6.85 (m, 2H), 6.35 (d, J=15.8 Hz, 1H), 6.08 (dt, J=15.8, 6.7 Hz, 1H), 5.90 (ddt, J=10.1, 17.1, 6.4 Hz, 1H), 5.10 (dq, J=17.1, 1.7 Hz, 1H), 5.05 (dq, J=10.1, 1.3 Hz, 1H), 3.79 (s, 3H), 2.94 ppm (tq, J=6.6, 1.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=158.7, 136.7, 130.4, 130.2, 127.1, 125.9, 115.4, 113.9, 55.2, 37.0 ppm; IR (NaCl plate, thin film): $\tilde{\nu}$=3003, 2956, 2934, 2908, 2835, 1637, 1607, 1511, 1462, 1441, 1296, 1248, 1175, 1106, 1035, 991, 967, 914, 839 cm^{-1}; HRMS-ESI: *m*/*z* calcd for $C_{12}H_{14}O$: 175.1117; found: 175.1119 $[M+H]^+$.

*1-Methoxy-4-(penta-1,3-dienyl)benzene (**3f**)*

^{1}H NMR (500 MHz, $CDCl_3$): distinguishable peaks are shown; (*E*)-isomer: δ=6.62 (dd, J=10.4, 15.7 Hz, 1H), 6.37 (d, J=15.6 Hz, 1H), 5.77 (dq, J=15.0, 6.8 Hz, 1H), 1.81 ppm (d, J=6.9 Hz, 3H); (*Z*)-isomer: δ=1.85 ppm (dd, J=1.8, 7.2 Hz, 3H).

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